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14. ABSTRACT Agiltron proposes a novel category of next generation CMC material comprising nano-size ceramic and carbon nanotube phases. In Phase I of this program, Agiltron successfully demonstrated the feasibility of the proposed approach through small-scale fabrication and characterization. In Phase II, Agiltron will optimize and scale up the fabrication process of the proposed nano-composite to achieve unprecedented performance. The proposed composite is intended to replace current ceramic and CMC materials to meet the next level military and commercial requirements for cost-effective mechanical component applications.					
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# New Generation Hybrid Carbon/Ceramic Nanocomposites

Sponsored by

Small Business Technology Transfer Research Program  
US Air Force

**Agiltron, Inc.**

**Progress Report  
September 1st, 2007**

**Contract No. FA9550-06-C-0136**

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## Phase II Objective

The Phase II objective is to make large size (>50 mm in diameter), fully dense, CNT/alumina composite nano-ceramics with 5 to 10 times enhanced mechanical toughness compared with pure phase ceramics. Another goal of this program is to scale-up the CNT/alumina powder synthesis capability to the multi-kilogram level with high CNT coating uniformity. We will correlate experiment results with established CMC models, and initiate a microstructural design and mechanical properties database for a class of hybrid carbon/ceramic nanocomposites. In the long run, the proposed composite is intended to replace current ceramic and CMC materials to meet the next advanced level military and commercial requirements for cost-effective mechanical component applications.

## Achievement Highlights in This Reporting Period

In this reporting period of this Phase II, we have extended the development scope of CNT coating process on Alumina nano-particles. We used alumina nano powder with a particle size of 20 nm, compared to larger nano-particles of 100~300 nm in dimension used in Phase I. We found that the CNT yield increased 70% on the small nano-particles with the same catalyst loading and CNT growth conditions. We also tried other reaction gas and growth temperature for high quality CNT growth. Secondly, we scaled up the SPS sintering process for large size CNT/alumina nanocomposite compacts (> 1" in diameter). Thirdly, we systematically evaluated the mechanical performance of CNT/alumina nanocomposites with different CNT concentration and sintering temperatures, and demonstrated Vicker hardness and fracture toughness increases of 8.4 % and 46.4 %, respectively, comparing with that of pure  $\text{Al}_2\text{O}_3$  sintered at the same temperature.

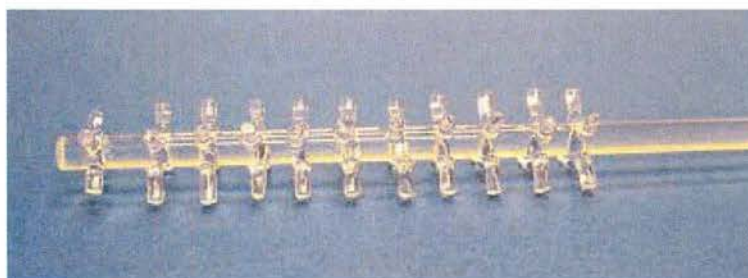
## Work Performed during This Reporting Period

### 1. Carbon Nanotube Growth on $\text{Al}_2\text{O}_3$ Nano-Particles with Different Concentrations

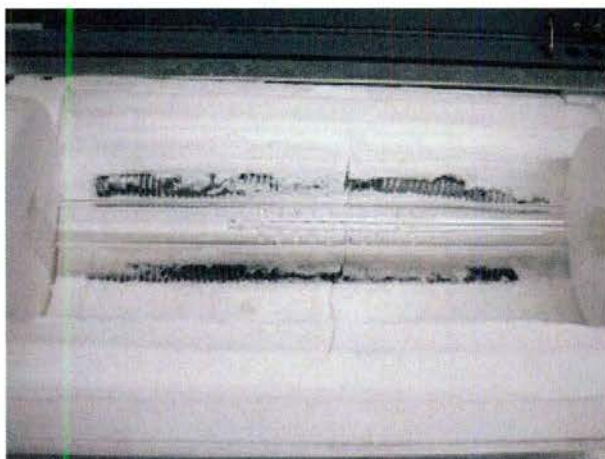
Two kinds of commercially available nano-sized  $\text{Al}_2\text{O}_3$  powders from Baikowski International was used. The coarse powder has particle size of 100~300 nm, while the fine powder has particle size of ~20 nm. CNT-alumina mixture powder was synthesized by chemical vapor deposition (CVD) method. Previous results indicate that CNTs can be grown by using  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  as a catalyst. In the current work,  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (98+%, Sigma-Aldrich) and  $\text{Al}_2\text{O}_3$  powder (CR30 High purity alumina powder, Baikowski International Corporation) were mixed in ethanol, followed by sonication for 15 min. Then the mixture was dried at 130 °C for overnight followed by grinding into a fine powder.

For CNT synthesis, alumina powder containing seven different cobalt contents ( $\text{Co}/\text{Al}_2\text{O}_3 = 0.5, 0.75, 1.0, 2.0, 3.0, 4.0$  and  $5.0$  wt%) was either dispersed in a molybdenum boat inserted in a tube furnace or placed directly in the reaction quartz tube for large amount synthesis. For large amount synthesis, the main modification in the CVD system was positioning a quartz stirrer,

which was activated to stir the powder to achieve a uniform exposure of the starting material to the reaction gases. The experimental set up is shown in Figure 1. In the following text, we refer to the growth by using boat as boat mode "BM" and the growth using stirrer as stirrer mode "SM". The stirring speed can be adjusted for an optimal result. Acetylene ( $C_2H_2$ ), argon (Ar), and hydrogen ( $H_2$ ) were introduced into the reaction chamber through distilled water bubbler for CNT growth. The synthesis of CNTs was carried out at  $750^\circ C$  for 15 min at gas ratio of  $C_2H_2:H_2:Ar = 100:400:600$  sccm.



(a)



(b)



(c)

Figure 1: A fused silica mechanical stirrer (a), the stirrer inside the reaction chamber (b), and a CVD system for CNT growth (c).

Figure 2 shows SEM image of the prepared pure alumina powders. The average size of the alumina particles  $0.1 \sim 0.3 \mu m$ , which is consistent with reported data by the manufacturer. Figure 3 (a), (b), (d)-(h) show the SEM images of CNT-alumina nanocomposites on  $Al_2O_3$  with different Co content ratios of 0.5, 0.75, 1.0, 2.0, 3.0, 4.0 and 5.0 wt%, respectively. For comparison, CNTs were also synthesized in BM on  $Al_2O_3$  with Co content ratios of 1.0 and 5.0%, and the image of the CNT-alumina composite from 1.0 wt% Co/ $Al_2O_3$  is shown in Figure 3 (c). In general, the content of CNTs in the composites increases with the increase of catalyst amount. In samples synthesized from 0.5 and 0.75 wt% Co/ $Al_2O_3$ , it is hard to find CNTs, and the distribution of CNTs is sparse as shown in Figure 3 (a) and (b). When the Co content increases to 1.0 and 2.0 wt%, the uniformly distributed CNTs and small bundles are formed in the alumina matrix as shown in Figure 3 (c), (d), and (e). Composites synthesized from 1.0 wt% Co/ $Al_2O_3$  by BM

(Figure 3 (c)) and SM (Figure 3 (d)) do not show notable difference in the uniformity and distribution of CNTs. As the Co content reaches to 3.0, 4.0, and 5.0 wt%, more CNTs and tangled clusters of CNTs are observed as shown in Figure 3 (f), (g) and (h). Due to the large quantity of CNTs in the composites synthesized from high Co concentrations, some alumina matrices are even wrapped around by these CNTs. The weight percentages of the CNTs in the  $\text{Al}_2\text{O}_3$  matrix were 3.19, 3.83, 5.04 (BM), 7.39, 8.25, 18.82, 19.10, and 20.50 wt% with respect to the Co contents of 0.5, 0.75, 1.0 (BM), 1.0, 2.0, 3.0, 4.0 and 5.0 wt%, respectively.



*Figure 2: SEM image of the original alumina powder used in this experiment. The alumina particle size is about 0.1 ~ 0.3 μm.*

The diameter of CNTs is about 10 ~ 40 nm, and their length is about 1 ~ 7 μm. The diameter of CNTs tends to increase with the increase of the cobalt catalyst concentration. Figure 4 shows the TEM images of CNTs grown on the 0.5, 1.0, and 5.0 wt% Co/ $\text{Al}_2\text{O}_3$  m. TEM results show that the nanotubes are multi-walled carbon nanotube (MWNTs) and usually have 10 ~ 40 graphite layers. Figure 5 presents the TEM images showing both the CNTs and the  $\text{Al}_2\text{O}_3$  nanoparticles, and it clearly shows that the CNTs are clean and curly and the  $\text{Al}_2\text{O}_3$  nanoparticles still keep their original size and do not grow bigger during the CNT growth. Some CNTs have closed tips (Figure 5) in which Co catalysts are usually capped inside (Figure 4 (d)). This finding may imply that the CNTs grown in the alumina are in tip growth mode.

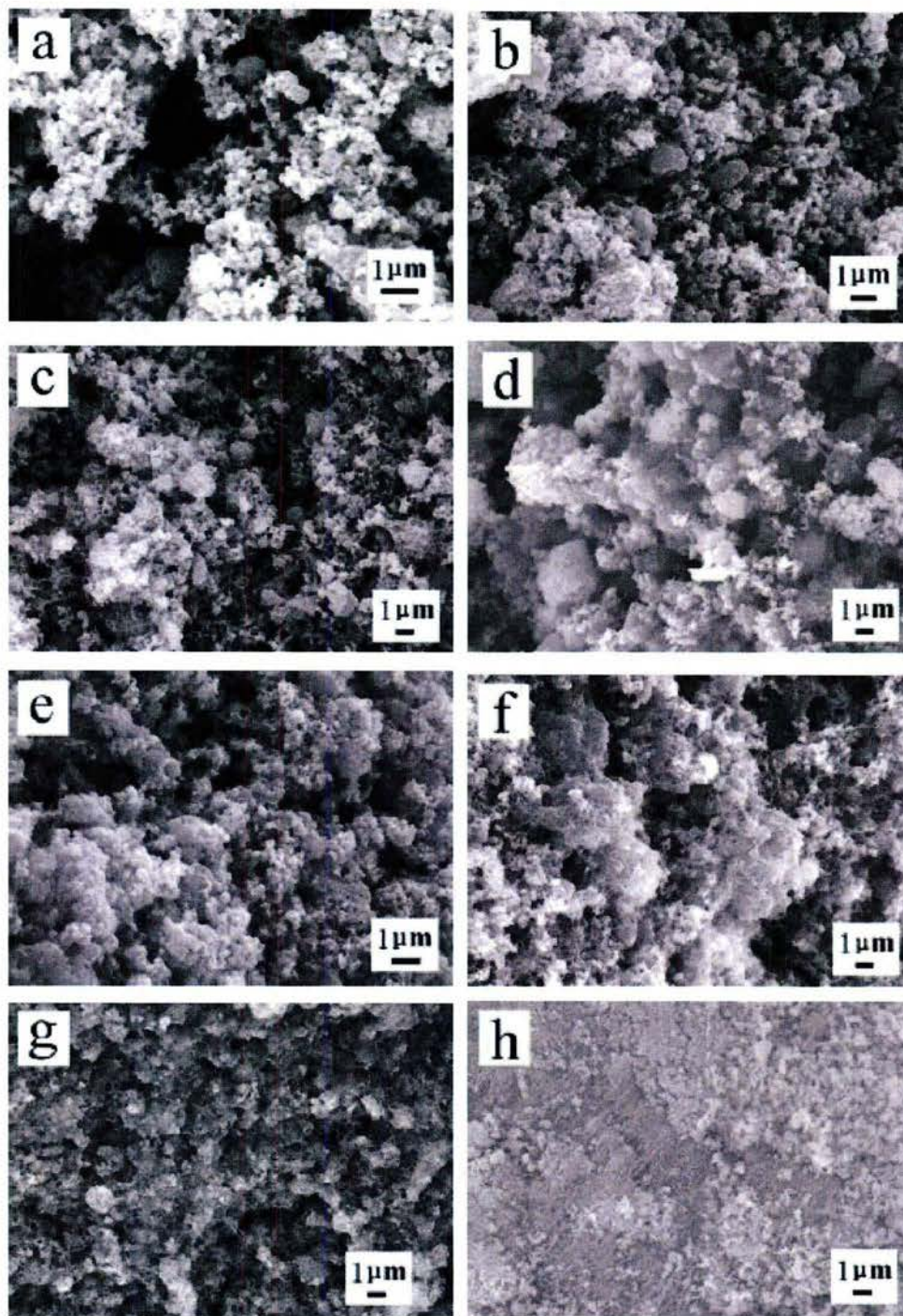


Figure 3: SEM images of the synthesized CNT-alumina nanocomposites with CNT content of (a) 3.19 wt% (on 0.5 wt% Co/Al<sub>2</sub>O<sub>3</sub>), (b) 3.83 wt% (on 0.75 wt% Co/Al<sub>2</sub>O<sub>3</sub>), (c) 5.04 wt% (on 1.0 wt% Co/Al<sub>2</sub>O<sub>3</sub>, BM), (d) 7.39 wt% (on 1.0 wt% Co/Al<sub>2</sub>O<sub>3</sub>), (e) 8.25 wt% (on 2.0 wt% Co/Al<sub>2</sub>O<sub>3</sub>), (f) 18.82 wt% (on 3.0 wt% Co/Al<sub>2</sub>O<sub>3</sub>), (g) 19.10 wt% (on 4.0 wt% Co/Al<sub>2</sub>O<sub>3</sub>), and (h) 20.50 wt% (on 5.0 wt% Co/Al<sub>2</sub>O<sub>3</sub>).

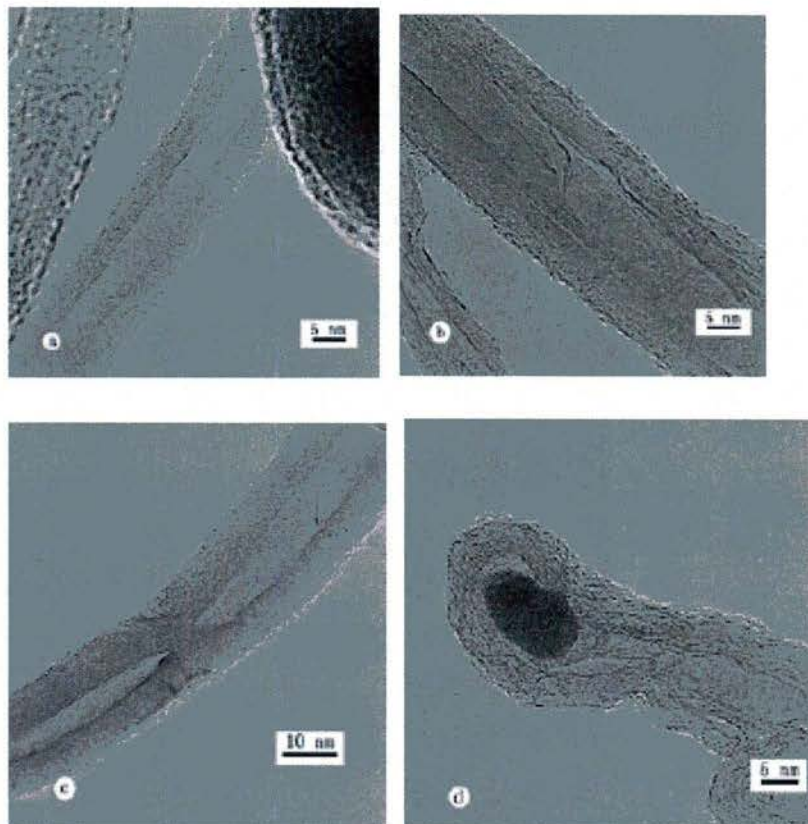


Figure 4: High resolution TEM images showing the microstructure of the as-grown CNTs Co/Al<sub>2</sub>O<sub>3</sub> with Co ratio of (a) 0.5 wt%, (b) 1.0 wt% (BM), (c) 1.0 wt% in, and (d) 5.0 wt% (BM).

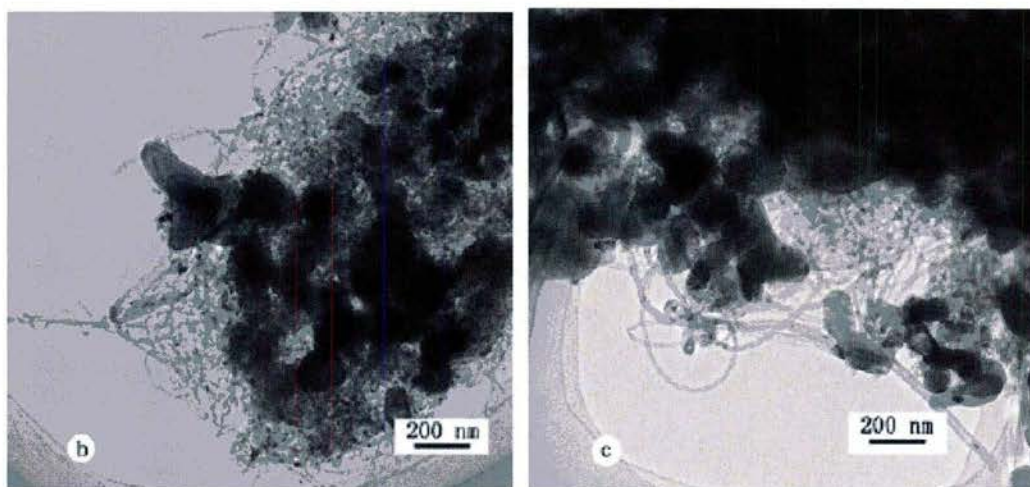


Figure 5: TEM images showing the morphology and size of CNTs and alumina particles in the samples containing CNTs of (b) 5.04 wt% (on 1.0 wt% Co/Al<sub>2</sub>O<sub>3</sub>, BM), and (c) 7.39 wt% (on 1.0 wt% Co/Al<sub>2</sub>O<sub>3</sub>, SM).

We also grew CNT on the fine powder. Figure 6 shows the SEM images of the synthesized composite. On nanometer-sized  $\text{Al}_2\text{O}_3$  particles, CNTs have very small diameters and are usually wrapping around the alumina particles. Comparing with the CNTs synthesized on the coarse alumina particles, the CNTs synthesized here are much smaller. The detailed morphology of the smaller tubes is hardly seen by SEM. Further structure characterization of the small CNTs by TEM is in process. On the coarse powder, the yield of CNTs from 1.0 wt%  $\text{Co}/\text{Al}_2\text{O}_3$  is about 7.0 wt%, in the current experiment the yield of CNTs from 1.0 wt%  $\text{Co}/\text{Al}_2\text{O}_3$  is about 12 wt%. It is expected that the higher concentration of small CNTs will have a positive significant impact on the mechanical property of the composite.



Figure 6: SEM images of the synthesized composite.

In order to get CNTs with high quality, such as a high degree of graphitization, we are testing a new method to synthesize better quality nanotubes on the small alumina grains. In the new method, methane ( $\text{CH}_4$ ) is used as carbon source and high temperature of  $1000^\circ\text{C}$  is used as the reaction temperature instead of using acetylene ( $\text{C}_2\text{H}_2$ ) as carbon source and a growth temperature of  $750^\circ\text{C}$ . This new method is based on our recent discovery, which shows that clean and smooth small nanotubes can be synthesized on  $\text{MgO}$  particles.

## 2. Sintering Scaling-up of CNT- $\text{Al}_2\text{O}_3$ Nanocomposite

We have sintered a CNT- $\text{Al}_2\text{O}_3$  nanocomposite large than 1" in diameter and 10mm in thickness using a scaled-up sintering process, as shown in Figure 7. CNT- $\text{Al}_2\text{O}_3$  nanopowder was placed in a graphite dies and sintered under vacuum in a SPS unit. The SPS conditions are as follows: an applied pressure 100 MPa, peak temperatures 1150 and  $1450^\circ\text{C}$ , heating rate  $100^\circ\text{C}/\text{min}$ , hold time at peak temperature 10 min, pulse duration 12 ms, and pulse interval 2 ms. Pure alumina specimen (CR30 High purity alumina powder, Baikowski International Corporation) was also sintered under the same SPS conditions at 1150 and  $1450^\circ\text{C}$  for comparison.

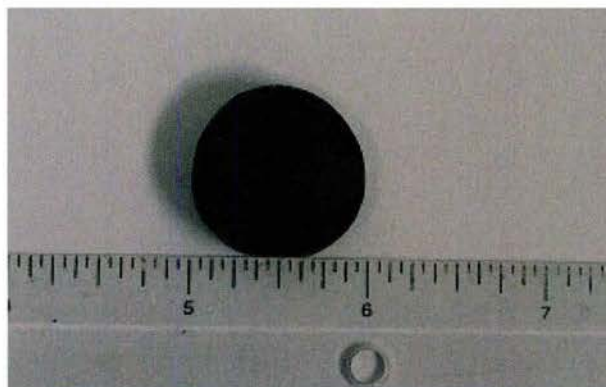


Figure 7: A SPS sintered CNT- $\text{Al}_2\text{O}_3$  nanocomposite.

### 3. Mechanical Performance Evaluation of CNT-Alumina Nanocomposites

After synthesis of CNT-alumina nanocomposite, spark plasma sintering (SPS) was employed to consolidate CNT-alumina nanocomposites. The density of the sintered CNT-alumina nanocomposite materials is measured by Archimedes method and is shown in Table I. For density measurement, deionized water was used as the immersion medium. Figure 8 is the graph of the densities as a function of CNT content in the specimens sintered at 1150 °C and 1450 °C. Comparing with the consolidated samples grown on 1.0 wt% Co/ $\text{Al}_2\text{O}_3$  by BM and SM, the density of SM grown sample is smaller than that of the BM grown sample, meaning that the CNT content in the SM grown sample is higher. This result indicates that stirring the Co/ $\text{Al}_2\text{O}_3$  during the synthesis can promote a high yield of CNTs. Figure 8 shows that density of all the CNT-alumina composites is lower than that of the pure alumina. At sintering temperature of 1150 °C or 1450 °C the density of the CNT-alumina increases with the increase of the CNT amount to a maximum then decreases. However, the maxima in the composites sintered at 1150 °C and 1450 °C are not in the composite with the same CNT content. Among the CNT-alumina composites sintered at 1150 °C, composite containing 8.25 wt% CNTs has the maximum density of 2.62 g/cm<sup>3</sup>. Among the CNT-alumina composites sintered at 1450 °C, composite containing 5.04 wt% CNTs has the maximum density of 3.35 g/cm<sup>3</sup>. In general, the densities of composites with the same CNT content increase significantly with the SPS temperature. It can also from the graph that the composite with 20.5 wt% CNTs has minimum density among the two groups of composites sintered at 1150°C and 1450°C. The above results indicate that the density of the CNT-alumina composites does not decrease linearly with the increase of the CNT amount. Furthermore, the maximum density of the CNT-alumina is determined by not only the amount of CNTs but also the sinter temperature. The maximum density we obtained so far is 84.4 % of the theoretical density of  $\text{Al}_2\text{O}_3$ . Ning et al reported that CNTs in  $\text{SiO}_2$  matrix act as a kind of solid impurity to prevent the flowing of matrix in the course of sintering, so here it seems CNTs in alumina composites hinder the densification of  $\text{Al}_2\text{O}_3$  matrix.<sup>1</sup> Because large quantity of CNTs was dispersed in the alumina matrix, they tended to form bundles or clusters, which may also

<sup>1</sup> Ning, J.W., Zhang, J.J., Pan, Y.B., and Guo, J.K., *Mater. Sci. & Eng. A* **357**, (2003) 392-396.

hinder the densification of the composite. An et al. reported a similar sintering behavior of CNT-alumina composites with CNT content over 10 wt%.<sup>2</sup>

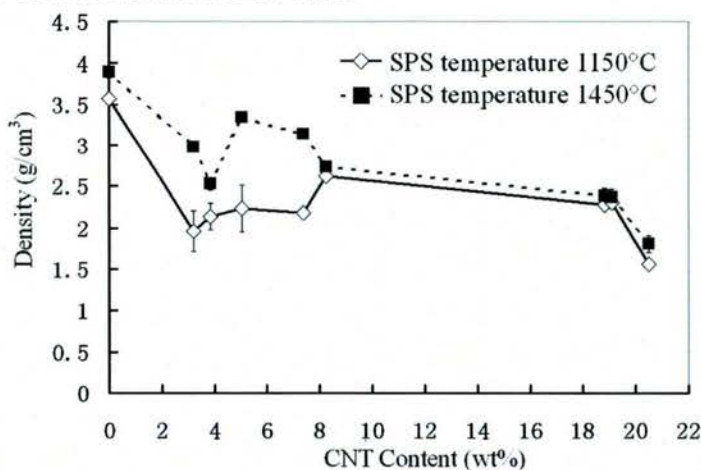


Figure 8: Graph of the density of CNT-alumina nanocomposite with respect to CNT content in the sample.

The Vicker hardness and fracture toughness of different CNT-Al<sub>2</sub>O<sub>3</sub> nanocomposites at sintering temperatures of 1150 and 1450 °C have been measured and are compared with those of pure alumina prepared at the same conditions, as shown in Table I, Figure 9 and Figure 10.

**Table I. Mechanical Properties of CNT-alumina Nanocomposites**

Percentage of catalyst in Al <sub>2</sub> O <sub>3</sub>	CNT content (wt%)	SPS temperature	Measured density (g/cm <sup>3</sup> )	Relative density (% TD)*	Hardness (GPa)	Fracture toughness (MPa <sup>1/2</sup> )
<b>0</b>	<b>0</b>	<b>1150°C</b>	<b>3.56 ± 0.02</b>	<b>89.7</b>	<b>8.60 ± 0.06</b>	<b>3.50 ± 0.07</b>
		<b>1450°C</b>	<b>3.90 ± 0.07</b>	<b>98.2</b>	<b>9.21 ± 0.32</b>	<b>3.88 ± 0.20</b>
<b>0.5</b>	<b>3.19</b>	<b>1150°C</b>	<b>1.96 ± 0.25</b>	<b>49.4</b>	<b>0.18 ± 0.04</b>	<b>n/a</b>
		<b>1450°C</b>	<b>2.98 ± 0.02</b>	<b>75.1</b>	<b>3.07 ± 1.73</b>	<b>3.83 ± 0.48</b>
<b>0.75</b>	<b>3.83</b>	<b>1150°C</b>	<b>2.14 ± 0.16</b>	<b>53.9</b>	<b>0.47 ± 0.41</b>	<b>n/a</b>
		<b>1450°C</b>	<b>2.53 ± 0.08</b>	<b>63.7</b>	<b>5.85 ± 0.34</b>	<b>4.09 ± 0.14</b>
<b>1.0</b>	<b>5.04 (BM)</b>	<b>1150°C</b>	<b>2.24 ± 0.28</b>	<b>56.4</b>	<b>2.22 ± 0.35</b>	<b>n/a</b>
		<b>1450°C</b>	<b>3.35 ± 0.01</b>	<b>84.4</b>	<b>9.69 ± 0.20</b>	<b>5.68 ± 0.16</b>

<sup>2</sup> An, J.W., and Lim, D.S., *J. Ceram. Proc. Res.* **3**, (2002) 201-204.

<b>1.0</b>	<b>7.39</b>	<b>1150°C</b>	<b>2.19 ± 0.02</b>	<b>55.2</b>	<b>2.29 ± 0.72</b>	<b>n/a</b>
		<b>1450°C</b>	<b>3.14 ± 0.02</b>	<b>79.1</b>	<b>9.98 ± 1.26</b>	<b>4.70 ± 0.74</b>
<b>2.0</b>	<b>8.25</b>	<b>1150°C</b>	<b>2.62 ± 0.01</b>	<b>66.0</b>	<b>2.22 ± 0.45</b>	<b>1.74 ± 0.42</b>
		<b>1450°C</b>	<b>2.73 ± 0.04</b>	<b>68.8</b>	<b>9.52 ± 1.88</b>	<b>2.47 ± 0.65</b>
<b>3.0</b>	<b>18.82</b>	<b>1150°C</b>	<b>2.28 ± 0.01</b>	<b>57.4</b>	<b>1.82 ± 0.38</b>	<b>1.30 ± 0.23</b>
		<b>1450°C</b>	<b>2.39 ± 0.02</b>	<b>60.2</b>	<b>9.11 ± 2.08</b>	<b>1.66 ± 0.22</b>
<b>4.0</b>	<b>19.1</b>	<b>1150°C</b>	<b>2.31 ± 0.02</b>	<b>58.2</b>	<b>1.01 ± 0.55</b>	<b>1.26 ± 0.41</b>
		<b>1450°C</b>	<b>2.37 ± 0.10</b>	<b>59.7</b>	<b>4.85 ± 1.24</b>	<b>1.32 ± 0.32</b>
<b>5.0</b>	<b>20.5 (BM)</b>	<b>1150°C</b>	<b>1.56 ± 0.02</b>	<b>39.3</b>	<b>0.07 ± 0.02</b>	<b>n/a</b>
		<b>1450°C</b>	<b>1.81 ± 0.10</b>	<b>45.6</b>	<b>0.09 ± 0.01</b>	<b>n/a</b>

Note: The SPS duration for all the samples is 10 min. TD denotes the theoretical density of  $\text{Al}_2\text{O}_3$ . BM denotes the boat growth mode of CNT- $\text{Al}_2\text{O}_3$  nanocomposites during CVD process.

Figure 9 shows the Vicker hardness of the samples as a function of the CNT content in the composite. It shows that the hardness is highly dependent on both the CNT concentration and the sintering temperature. At sintering temperature 1150 °C, the hardness of the composites with all CNT contents is much lower than that of pure  $\text{Al}_2\text{O}_3$  (8.60 GPa) while at 1450 °C the hardness of some samples is higher than that of pure  $\text{Al}_2\text{O}_3$  (9.21 GPa). For example, at sintering temperature 1450 °C, the samples with CNT concentrations of 5.04 wt% (grown from 1.0 wt% Co/ $\text{Al}_2\text{O}_3$ , BM), 7.39 wt% (1.0 wt% Co/ $\text{Al}_2\text{O}_3$ , SM), and 8.25 wt% (grown from 2.0 wt% Co/ $\text{Al}_2\text{O}_3$ , SM) have a hardness 9.69, 9.98, and 9.52 GPa, respectively, which is about 5.2, 8.4 and 3.4 % increase from the hardness of pure  $\text{Al}_2\text{O}_3$  (9.21 GPa). If the CNT concentration is either very low or very high, the hardness of the composite will be lower than that of pure  $\text{Al}_2\text{O}_3$ . In Fig.2.2, the hardness decreases rapidly when the CNT concentration increases from 0 to 3.19 wt% in the composites, then it increases immediately with CNT concentration from 3.19 to 7.39 wt%, then it decreases gradually with CNT concentration from 7.39 to 18.2 wt% CNTs, then it decreases sharply again with the CNT contraction from 18.2 to 20.50 wt%. The maximum hardness of the samples sintered at 1150 °C and 1450 °C will be reached when the CNT concentration is in the range of 5.00–8.50 wt%, and they are 2.29 GPa at 1150 °C and 9.98 GPa at 1450 °C when the CNT concentration is 7.39 wt%. Additionally, the Table I and Fig. 2.2 also show that the hardness increases dramatically with the sintering temperature. The 3.19 wt% CNT- $\text{Al}_2\text{O}_3$  has a hardness of 3.07 GPa at 1450 °C, a huge increase from 0.18 GPa at 1150 °C. The 7.39 wt% CNT- $\text{Al}_2\text{O}_3$  also has the significant increase in hardness with sintering

temperature, from 2.29 GPa at 1150 °C to 9.98 GPa at 1450 °C. Comparing with SM and BM grown samples, their hardness is very close. For example, at sintering temperature 1450 °C, the hardness of 5.04 wt% (grown from 1.0 wt% Co/Al<sub>2</sub>O<sub>3</sub>, BM) and 7.39 wt% (grown from 1.0 wt% Co/Al<sub>2</sub>O<sub>3</sub>, SM) is 9.69 GPa and 9.98 GPa, respectively.

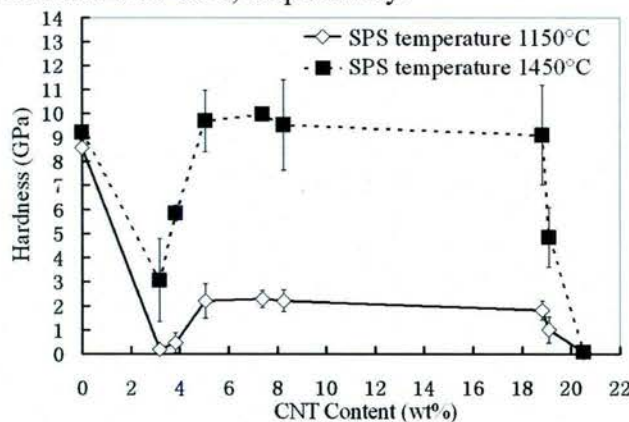


Figure 9: Graph of Vicker hardness of CNT-alumina nanocomposite as a function of the CNT content in the sample.

The fracture toughness of CNT-alumina nanocomposites are listed in Table I and plotted in Figure 10. For CNT-Al<sub>2</sub>O<sub>3</sub> nanocomposites sintered at temperature 1150°C, the fracture toughness of some specimens (1.74, 1.30, and 1.26 MPam<sup>1/2</sup> for 8.25, 18.82, and 19.10 wt% CNT-Al<sub>2</sub>O<sub>3</sub> respectively) are much lower than that of pure Al<sub>2</sub>O<sub>3</sub> (3.50 MPam<sup>1/2</sup>) and some of them (3.19, 3.83, 5.04 and 7.39 wt% CNT-Al<sub>2</sub>O<sub>3</sub>) even could not be determined due to the soft texture of samples at this SPS temperature. At sintering temperature 1450°C, the fracture toughness changes notably with the CNT percentage in the composite with a maximum toughness at 5 wt% CNTs, as shown in Figure 10. The 3.19 wt% CNT-Al<sub>2</sub>O<sub>3</sub> has a fracture toughness of 3.83 MPam<sup>1/2</sup>, which is very close to the fracture toughness 3.88 MPam<sup>1/2</sup> of pure Al<sub>2</sub>O<sub>3</sub>. The 5.04 wt% (BM) and 7.39 wt% (SM) CNT-Al<sub>2</sub>O<sub>3</sub> composites synthesized on 1.0 wt% Co-Al<sub>2</sub>O<sub>3</sub> have toughness of 5.68 MPam<sup>1/2</sup> and 4.70 MPam<sup>1/2</sup>, respectively, which are about 46.4 % and 21.1 % increases with respect to the fracture toughness of pure alumina. As the CNT content in the sample increases, the fracture toughness decreases tremendously, indicating that excessive CNTs will not enhance but may compromise toughness of the alumina. It was reported that there was no noted reinforcing effect in the *in situ catalytic grown* and hot pressed CNT-Al<sub>2</sub>O<sub>3</sub> nanocomposites and the fracture toughness of CNT-Fe-Al<sub>2</sub>O<sub>3</sub> nanocomposites was similar to that of pure alumina.<sup>3</sup> This result is ascribed to the damage of CNTs during hot pressing, which is usually operated at temperature as high as 1600 °C for duration as long as 1 hour.<sup>4</sup> Contrast to the hot pressing, the SPS takes place for only 10 minutes in our experiments. The short SPS duration may minimize the damage to the CNTs while achieve high density.

Comparing with graphs of density (Figure 8), Vicker hardness (Figure 9), and fracture toughness (Figure 10), one can find that the Vicker hardness, fracture toughness, and density

<sup>3</sup> Peigney, A., Laurent, Ch., Flahaut, E., and Rousset, A., *Ceram. Int'l.* **26**, (2000) 677-683.

<sup>4</sup> Flahaut, E., Peigney, A., Laurent, Ch., Marlière, Ch., Chastel, F., and Rousset, A., *Acta. Mater.* **48**, (2000) 3803-3812

change with the CNT content in the similar trend. They all have maximum values in the range of CNTs of 4 - 8wt%. At SPS temperature 1450 °C, samples containing CNTs of 5.04 wt% (BM) and 7.39 wt% (SM) have the first and second high densities of 3.35 g/cm<sup>3</sup> and 3.14 g/cm<sup>3</sup>, respectively, among the samples sintered at the same temperature. These two samples also have obtained the first and the second highest hardness of 9.69 GPa (BM) and 9.98 GPa (SM) and toughness of 5.68 MPam<sup>1/2</sup> (BM) and 4.70 MPam<sup>1/2</sup> (SM), respectively. At SPS temperature 1150 °C, the sample containing 8.25 wt% CNTs has the highest density of 2.62 g/cm<sup>3</sup>, a high hardness of 2.22 GPa (close to the highest 2.29 GPa for 7.39 wt% CNT-Al<sub>2</sub>O<sub>3</sub> sample), and the highest toughness of 1.74 MPam<sup>1/2</sup>. The sample containing 20.5 wt% CNT has the lowest density, hardness and toughness at any sintering temperature. This may be ascribed to the low extent of bonding of carbon nanotubes in the alumina matrix as a function of nanocomposite density.<sup>5</sup>

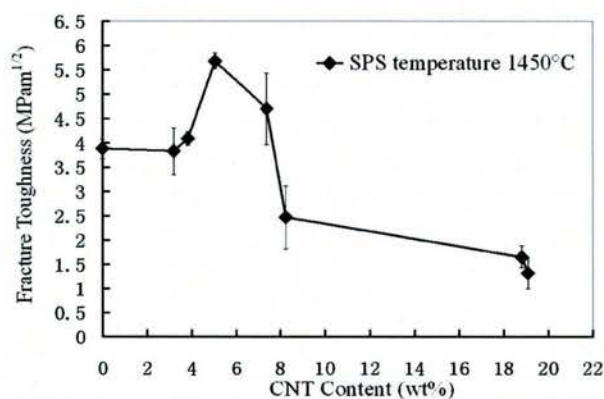


Figure 10: Fracture toughness of the pure alumina and different CNT-alumina nanocomposites sintered at temperature 1450°C.

Figure 11 shows the fracture surface of sintered CNT-Al<sub>2</sub>O<sub>3</sub> nanocomposite. The densities of all the CNT-Al<sub>2</sub>O<sub>3</sub> nanocomposites sintered at 1150°C are much lower than that of pure alumina. The 5.04 and 7.39 wt% CNT-Al<sub>2</sub>O<sub>3</sub> samples sintered at 1450°C have the highest relative density of about 84 % of theoretical density of alumina. Figure 11 (d) shows the fracture surface of the 7.39 wt% CNT-Al<sub>2</sub>O<sub>3</sub>. It can be seen that some of CNTs are entangled or encapsulated with alumina grains, and form an entangling network, but on the same sample, it is also observed that in some sites the entangling network become the loose network. For comparison, Figure 11 (c) shows the 7.39 wt% CNT-Al<sub>2</sub>O<sub>3</sub> sintered at 1150 °C. The relative density of this sample is only 55.2 % of that of the pure alumina. In Figure 11 (c), it is hard to find the entangling network, and most of CNTs are lack of interfacial contact. The same situation is also found in other samples. It is possible that the density of CNT-alumina nanocomposite depends on the bonding between the nanotubes and their surrounding matrix system. The finding suggests that the interfacial contact bonding is also one of the important factors in determining the fracture toughness.

<sup>5</sup> Zhan, G.D., Kuntz, J.D., Wan, J. and Mukherjee, A.K., *Nature Mater.* **2**, (2003) 38-42.

Figure 11 shows the fracture surfaces of the 3.19, 7.39, and 19.10 wt% CNT-alumina nanocomposites sintered at 1150 °C and 1450 °C. The images showed that CNTs survived from the quick high temperature SPS consolidation. Comparing the SEM images of CNT-alumina composites before SPS consolidation (Figure 3), the morphology, quantity, and distribution of CNTs in the consolidated samples have no significant change, and CNTs are still homogeneously dispersed between the alumina grains. Comparing image (a) and (b), (c) and (d), (e) and (f) in Figure 11, one can find that the composites sintered at low temperature of 1150 °C has high porosity while the composites sintered at high temperature of 1450 °C has low porosity. The intimate contact between CNTs and alumina grains in composites sintered at high temperature will contribute to high toughness of the composites. In addition to the sintering temperature, the concentration of CNTs in the CNT- $\text{Al}_2\text{O}_3$  will also greatly affect the mechanical properties of the composites. In the composite with 3.19 wt% CNTs (Figure 11 (a) and (b)), the low concentration CNTs results in a very small change in the toughness of the nanocomposite. In composite with 7.39 wt% CNTs (Figure 11 (c) and (d)), the proper amount CNTs form entangling networks within the alumina grains and improve the mechanical properties. In composite with 19.10 wt% CNTs (Figure 11 (e) and (f)), large amount of CNTs form clusters which prohibit the direct contact of every CNTs to alumina grains. As a result, the mechanical properties of the CNT-alumina composites can not be enhanced at all by the CNTs or even weaken the mechanical property of the alumina.

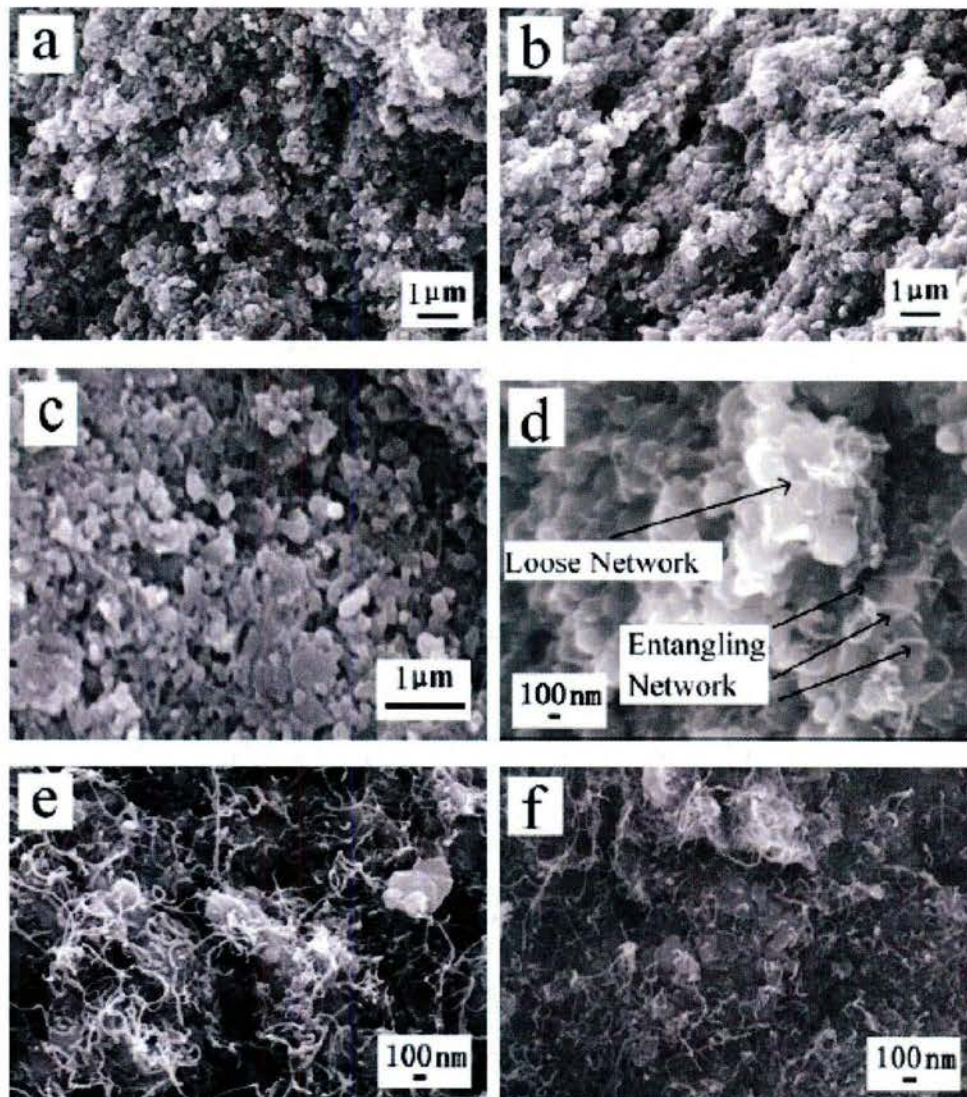


Figure 11: Fracture surfaces of three CNT- $\text{Al}_2\text{O}_3$  nanocomposites sintered at different temperatures. The 3.19 wt% CNT- $\text{Al}_2\text{O}_3$  sintered at (a) 1150°C and (b) 1450 °C; the 7.39 wt% CNT- $\text{Al}_2\text{O}_3$  sintered at (c) 1150 °C and (d) 1450 °C; the 19.1 wt% CNT- $\text{Al}_2\text{O}_3$  sintered at (e) 1150 °C and (f) 1450 °C.

Figure 12 is an enlarged image of the fracture surface of the 7.39 wt% CNT- $\text{Al}_2\text{O}_3$  composite sintered at 1450 °C. The pull-out of CNTs which were trapped in alumina matrix grains during SPS process has been observed. The high aspect ratio and enormous specific surface area (up to 1315  $\text{m}^2/\text{g}$ ) of CNTs provide a high potential for toughening through pull-outs. The work of the interfacial friction between CNTs and alumina matrix grains and part of the fracture energy are related to these parameters.<sup>6</sup> The pull-outs indicate the existence of weak interfacial strength between CNTs and alumina matrix grains, which contributes to the

<sup>6</sup> Wichmann, M.H.G., Sumflesh, J., Fiedler, B., Gojny, F.H., and Schulte, K., *Mech. Composite Mater.* **42**, (2006) 567–582.

reinforcement. The cutting breakages and outcrops of CNTs can also be clearly seen in Figure 12. The breakage is possibly due to the defects of CNTs, such as the kinks as shown in the TEM image in Figure 4. The defects may reduce the stiffness of CNTs, and make CNTs easily break down in these sites when they meet the stress transferred through the matrix. The fracture is mostly intergranular for the samples with different CNT concentrations while the fracture of pure alumina is essentially transgranular. The reinforcement involving the transgranular fracture is not desired. CNT bundles could dissipate some fracture energy for composite with micrometer sized grains, while the porosity associated with the CNT bundles may impair the reinforcement. In any fiber-reinforced composites, one of the keys to an efficient reinforcement is that the fiber-matrix interface is not too weak but also not too strong so that the decohesion of the CNT-matrix interfaces can allow some energy absorption under stress via CNT pull-outs.

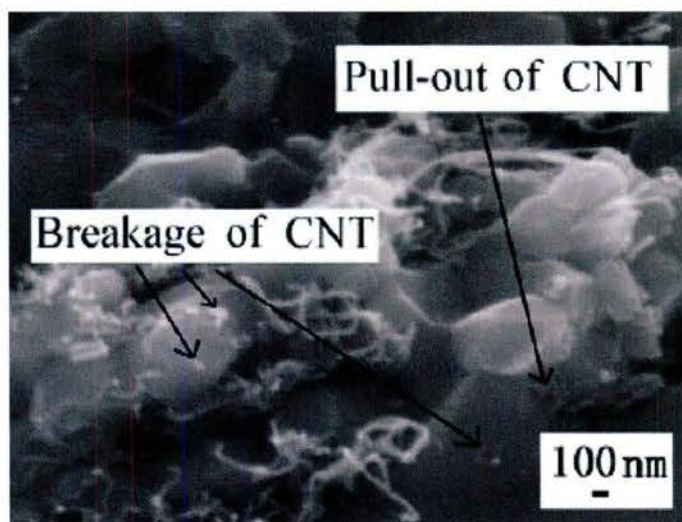


Figure 12: Fracture surface of the 7.39 wt% CNT-alumina nanocomposite sintered at 1450 °C showing the breakage and pull-out of CNTs under stress.

The mechanical properties of the CNT-alumina nanocomposite are affected by several factors. First, the quantity and uniformity of CNTs in the nanocomposites will greatly affect the hardness and toughness of the composites. As shown in Figure 9 and Figure 10, at the minimum concentration of 3.19 wt% of CNTs, both the hardness and toughness of the composite are lower than those of the pure alumina. With the increase of the CNT concentration, the hardness and toughness also increase to maxima then decrease. Comparing with the pure alumina, maximum 8.4 % increase in Vicker hardness and maximum 46.4 % increase in fracture toughness have been obtained from composites with 7.39 wt% and 5.04 wt% CNTs. Small amount of CNTs is not sufficient for improving the hardness and toughness of the CNT-alumina composite while excessive amount CNTs will hinder the densification resulting in low density, hardness, and toughness. Second, the quality of CNT will significantly affect the toughness of the composites. In our CNT-alumina nanocomposites, most of the CNTs grown are multi-walled CNTs (MWNTs). In MWNTs, the graphene layers are only linked through weak van der Waals forces, and the inner layers can move easily without too much load. When the MWNTs are embedded in the alumina matrix, only their outer layers can transfer load from matrix to nanotubes since their

inner layers can not bond to the alumina matrix and contribute little to the load transfer. Comparing with single-walled CNTs (SWNTs), MWNTs may contain more defects in structure, which will reduce the stiffness of CNTs in alumina. Third, the consolidation conditions of the nanocomposites are very important in improving the hardness and toughness. To enhance these properties, a dense nanocomposite with undamaged CNTs is necessary. In this research, two different sintering temperatures, 1150 °C and 1450 °C, were tried to consolidate the CNT-alumina nanocomposites. At 1450 °C, the highest density, hardness and toughness have been obtained. Forth, it is expected that the sintering duration is also a very important factor that affects the hardness and toughness of the composites. In the current research, we have applied SPS for 10 minutes for consolidating CNT-alumina powders. We will investigate in detail the effect of the SPS duration on the mechanical properties of CNT-alumina nanocomposite.

## Conclusion

CNT-alumina nanocomposites have been successfully synthesized using CVD method and densified by SPS. Multi-walled nanotubes (MWNTs) with diameters in the range of 10 ~ 40 nm have directly grown on the alumina nanoparticles, and the as-grown CNTs are homogeneously distributed within the alumina matrix.

The density of the sintered CNT-alumina nanocomposites is lower than that of pure alumina and decreases with the increase of CNT content in the composite. Respectively, maximum 9.98 GPa in hardness and maximum 5.68 MPam<sup>1/2</sup> in fracture toughness have been measured in 7.39 wt% and 5.04 wt% CNT-Al<sub>2</sub>O<sub>3</sub> nanocomposites sintered at 1450 °C. Comparing with the hardness and toughness of pure Al<sub>2</sub>O<sub>3</sub>, increases of 8.4 % in hardness and 46.4 % in toughness have been achieved in our CNT-alumina composites. The entangling network between CNTs and alumina grains and the pull-outs of CNTs at fracture surface contribute to the reinforcement in the mechanical properties. Either very low or very high concentration of CNTs in the composite will compromise the mechanical properties of the ceramic. The optimal concentration of CNTs in the composite is between 5-7 wt%. The sintering temperature affects significantly the mechanical properties of the CNT-alumina composites, composites sintered at 1450 °C has higher density, hardness, and toughness than those sintered at 1150 °C.